

Solvent-dependent selective cation exchange in anionic frameworks based on cobalt(II) and triphenylamine linkers: reactor-dependent synthesis and sorption properties

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Supplementary Information

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1 Reactor vessels



Fig. S1: Reactor vessels utilized in MOF syntheses: (Left) 110 mL Perkin Elmer acid digestion bomb for MIL-144. (Right) 23 mL Parr acid digestion bomb for JUMP-2.

2 Analytical data for cation-exchanged samples

2.1 Exchange with lithium ions

JUMP-2(Li)E

Analytical Data for $[(Me_2NH_2)Li[Co(ntb)Cl] \cdot C_2H_5OH \cdot 1.5 DMF]_n$

Anal. Calcd for $C_{29.5}H_{36.5}ClCoLiN_{3.5}O_{8.5}$ ($677.45 \text{ g mol}^{-1}$):

C 52.30, H 5.43, N 7.24 %. Found: C 52.10, H 5.35, N 7.39 %.

Selected IR (ATR, cm^{-1}): 1651w, 1591s, 1506m, 1370s, 1313s, 1271s, 1174s, 1103m, 1045m.

JUMP-2(Li)D

Analytical Data for $[(Me_2NH_2)Li[Co(ntb)Cl] \cdot C_2H_5OH \cdot DMF \cdot H_2O]_n$

Anal. Calcd for $C_{28}H_{35}ClCoLiN_3O_9$ ($658.92 \text{ g mol}^{-1}$):

C 51.04, H 5.35, N 6.38 %. Found: C 51.10, H 5.61, N 6.17 %.

Selected IR (ATR, cm^{-1}): 1652w, 1591s, 1506m, 1372s, 1313s, 1270s, 1173s, 1088m, 1045m.

MIL-144(Li)E

Analytical Data for $[Li_2[Co_5(ntb)_4(H_2O)_3(C_2H_5OH)]] \cdot 17 H_2O]_n$

Anal. Calcd for $C_{86}H_{94}Co_5Li_2N_4O_{45}$ ($2212.21 \text{ g mol}^{-1}$):

C 46.69, H 4.28, N 2.53 %. Found: C 46.67, H 4.20, N 2.36 %.

Selected IR (ATR, cm^{-1}): 1589s, 1535m, 1506m, 1378vs, 1313s, 1270s, 1176s, 1087m, 1045m.

MIL-144(Li)D

Analytical Data for $[(Me_2NH_2)Li[Co_5(ntb)_4(H_2O)_3(C_2H_5OH)]]_n \cdot 3 C_2H_5OH \cdot 2 H_2O$

Anal. Calcd for $C_{94}H_{90}Co_5LiN_5O_{33}$ ($2119.34 \text{ g mol}^{-1}$):

C 53.27, H 4.28, N 3.30 %. Found: C 53.18, H 4.41, N 3.20 %.

Selected IR (ATR, cm^{-1}): 1589s, 1536m, 1505m, 1376vs, 1312s, 1269s, 1175s, 1088m, 1043m.

2.2 Exchange with europium(III) ions

JUMP-2(Eu)E

Analytical Data for $[(\text{MeNH}_2)_3\text{Eu}(\text{Co}(\text{ntb})\text{Cl})_3] \cdot 3 \text{C}_2\text{H}_5\text{OH} \cdot 6 \text{DMF}$

Anal. Calcd for $\text{C}_{93}\text{H}_{120}\text{Cl}_3\text{Co}_3\text{EuN}_{12}\text{O}_{27}$ ($2273.13 \text{ g mol}^{-1}$):

C 49.14, H 5.32, N 7.39 %. Found: C 49.52, H 5.03, N 7.22 %.

Selected IR (ATR, cm^{-1}): 1653w, 1594s, 1505m, 1367s, 1313s, 1268s, 1170s, 1103m.

JUMP-2(Eu)D

Analytical Data for $[\text{Eu}_2(\text{Co}(\text{ntb})\text{Cl})_3] \cdot 9 \text{C}_2\text{H}_5\text{OH} \cdot 3 \text{DMF}$

Anal. Calcd for $\text{C}_{90}\text{H}_{111}\text{Cl}_3\text{Co}_3\text{Eu}_2\text{N}_6\text{O}_{30}$ ($2343.95 \text{ g mol}^{-1}$):

C 46.12, H 4.77, N 3.59 %. Found: C 46.08, H 4.91, N 3.77 %.

Selected IR (ATR, cm^{-1}): 1591s, 1535m, 1506m, 1376vs, 1313s, 1271s, 1174s, 1088m, 1043s.

MIL-144(Eu)E

Analytical Data for $[(\text{Me}_2\text{NH}_2)_3\text{Eu}[\text{Co}_5(\text{ntb})_4(\text{H}_2\text{O})_3(\text{C}_2\text{H}_5\text{OH})]_3] \cdot 54 \text{H}_2\text{O} \cdot 18 \text{C}_2\text{H}_5\text{OH}$

Anal. Calcd for $\text{C}_{300}\text{H}_{420}\text{Co}_{15}\text{EuN}_{15}\text{O}_{156}$ ($7768.51 \text{ g mol}^{-1}$):

C 46.38, H 5.45, N 2.70 %. Found: C 46.37, H 5.68, N 2.44 %.

Selected IR (ATR, cm^{-1}): 1589s, 1529m, 1504m, 1382vs, 1312s, 1270s, 1175s, 1086m, 1042s.

MIL-144(Eu)D

Analytical Data for $[(\text{Me}_2\text{NH}_2)_3\text{Eu}[\text{Co}_5(\text{ntb})_4(\text{H}_2\text{O})_3(\text{C}_2\text{H}_5\text{OH})]_3] \cdot 42 \text{H}_2\text{O} \cdot 18 \text{C}_2\text{H}_5\text{OH}$

Anal. Calcd for $\text{C}_{300}\text{H}_{396}\text{Co}_{15}\text{EuN}_{15}\text{O}_{144}$ ($7552.33 \text{ g mol}^{-1}$):

C 47.71, H 5.29, N 2.78 %. Found: C 47.75, H 5.20, N 2.94 %.

Selected IR (ATR, cm^{-1}): 1590s, 1535m, 1505m, 1382vs, 1312s, 1271s, 1175s, 1087m, 1043s.

3 Additional structure information for JUMP-2

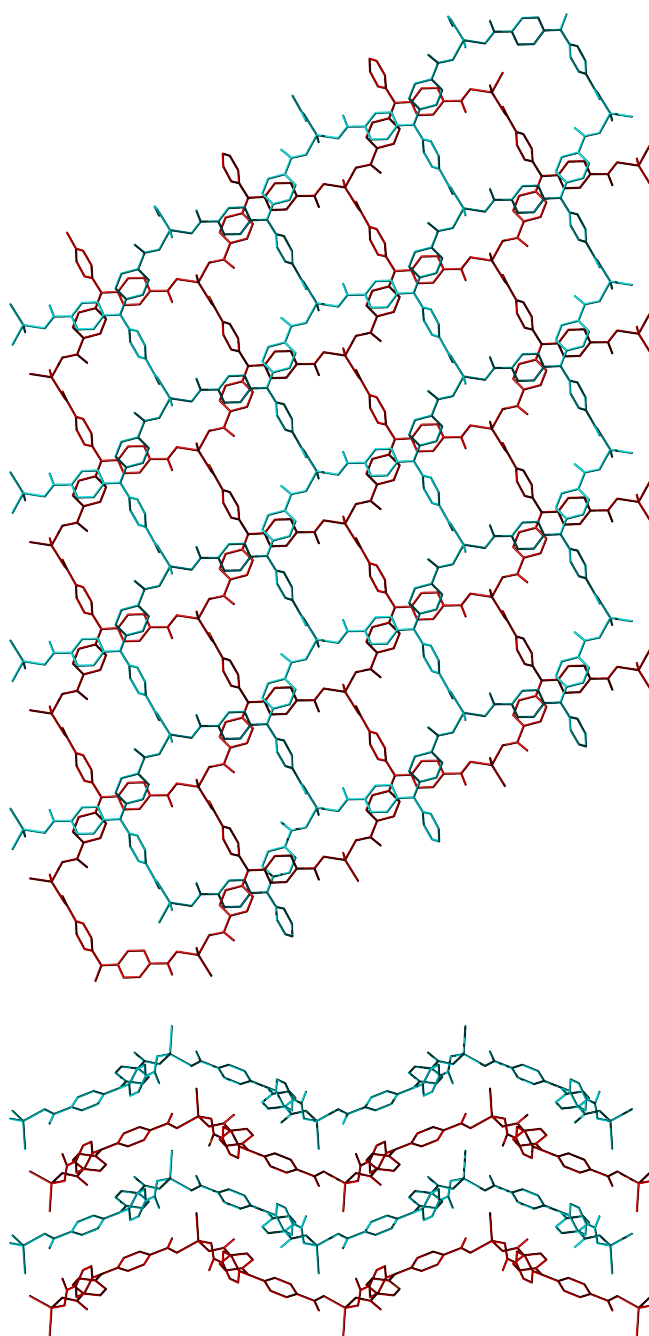


Fig. S2: 2D layered arrangement of the anionic framework in JUMP-2 showing the staggered arrangement: (Top) View along the $[010]$ direction. (Bottom) Side view along the $[100]$ direction.

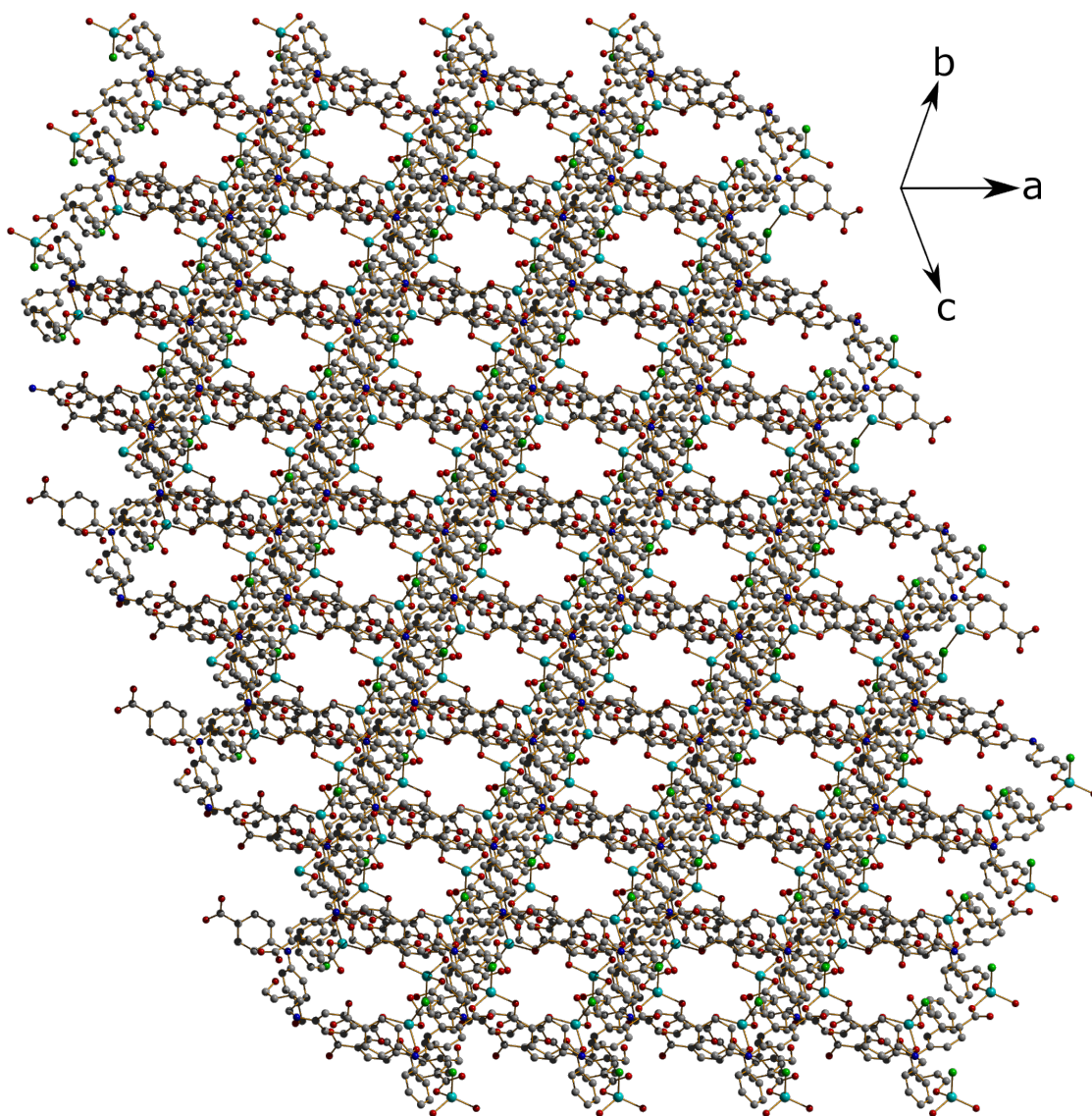


Fig. S3: 1D channels in the anionic framework of JUMP-2 viewed along $[12\bar{1}]$ direction.

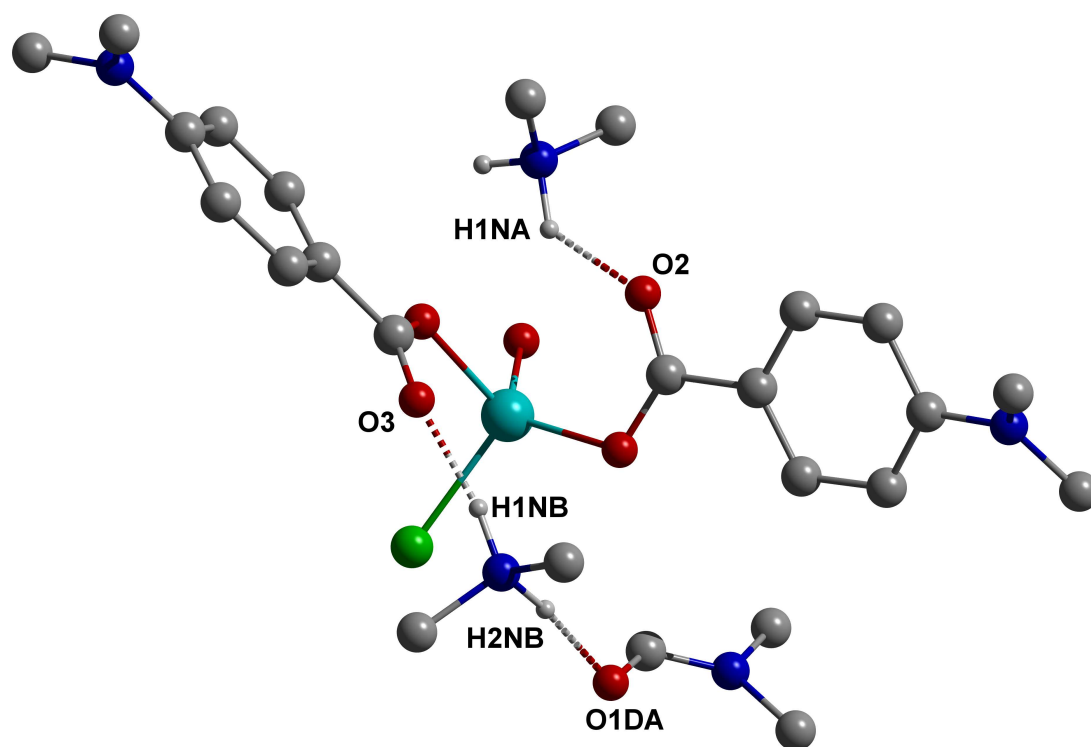


Fig. S4: Representation of the hydrogen bonding interactions for a cutout of the anionic framework of JUMP-2. Pertinent data: $O_2 \cdots N_1EA$ 271.7(5), $O_3 \cdots N_1EB$ 271.1(5), $O_1DA \cdots N_1EB$ 277.0(9) pm.

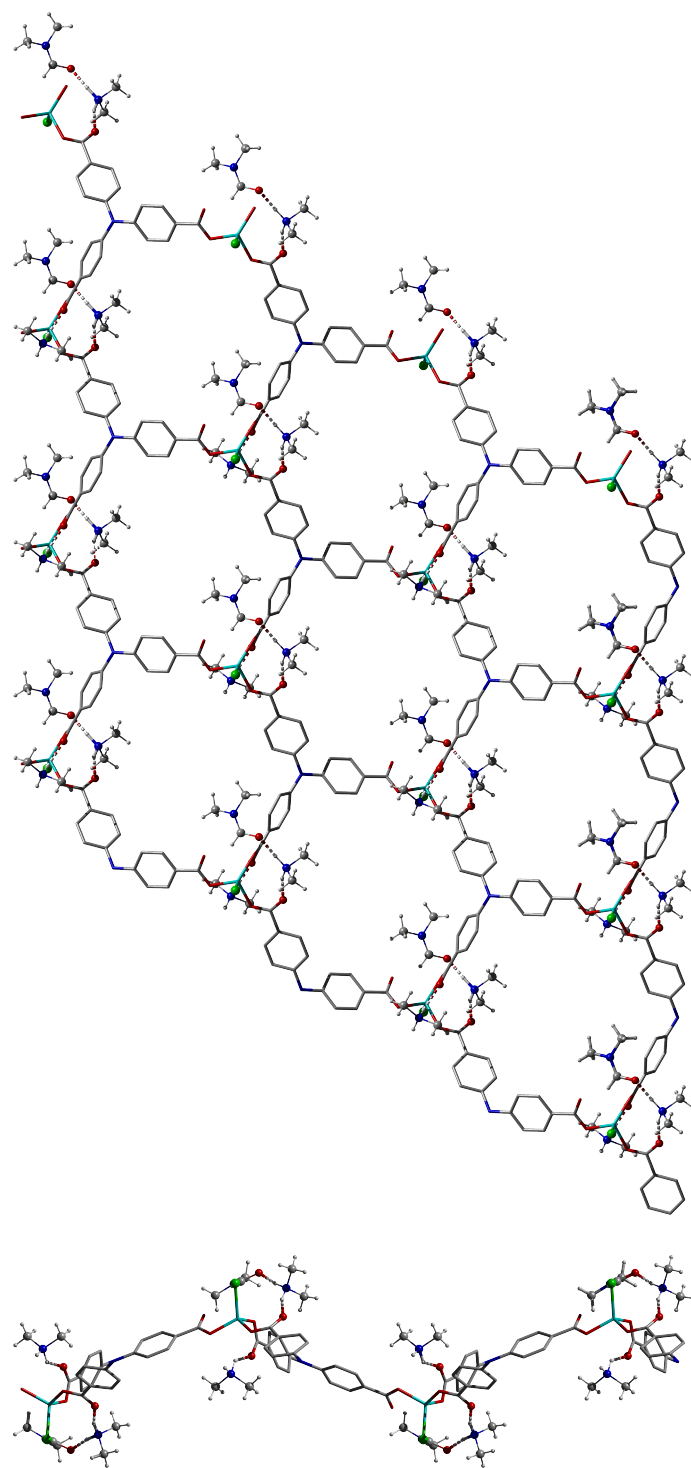


Fig. S5: Representation of the hydrogen bonding around the 2D layers in JUMP-2 viewed along [010] direction: (Top) View along the [010] direction. (Bottom) Side view of one layer along the $[100]$ direction.

4 Topological analysis

4.1 Topological analysis for JUMP-2

Ideal space group is $P6mm$.

Table S1: Coordination sequences for JUMP-2 (topological density $TD_{10} = 166$)

Vertex	CS ₁	CS ₂	CS ₃	CS ₄	CS ₅	CS ₆	CS ₇	CS ₈	CS ₉	CS ₁₀
V1	3	6	9	12	15	18	21	24	27	30
V2	3	6	9	12	15	18	21	24	27	30

Table S2: Vertex Symbols for JUMP-2

Vertex	Vertex symbol	Extended Point Symbol
V1	[6 ³]	[6.6.6]
V2	[6 ³]	[6.6.6]

4.2 Topological analysis for MIL-144

Ideal space group: $R\bar{3}c$.

Table S3: Coordination sequences for MIL-144 (topological density $TD_{10} = 1192$)

Vertex	CS ₁	CS ₂	CS ₃	CS ₄	CS ₅	CS ₆	CS ₇	CS ₈	CS ₉	CS ₁₀
V1	3	13	16	52	45	134	103	257	171	418
V2	6	8	32	30	90	76	206	140	342	218

Table S4: Vertex Symbols for MIL-144

Vertex	Vertex symbol	Extended Point Symbol
V1	[4 ² .6]	[4.4.6]
V2	[4 ⁴ .6 ² .8 ⁸ .10]	[4.4.4.4.6.6.8 ₂ .8 ₃ .8 ₃ .8 ₄ .8 ₇ .8 ₇ .8 ₇ .10 ₁₄]

4.3 Tiling of MIL-144

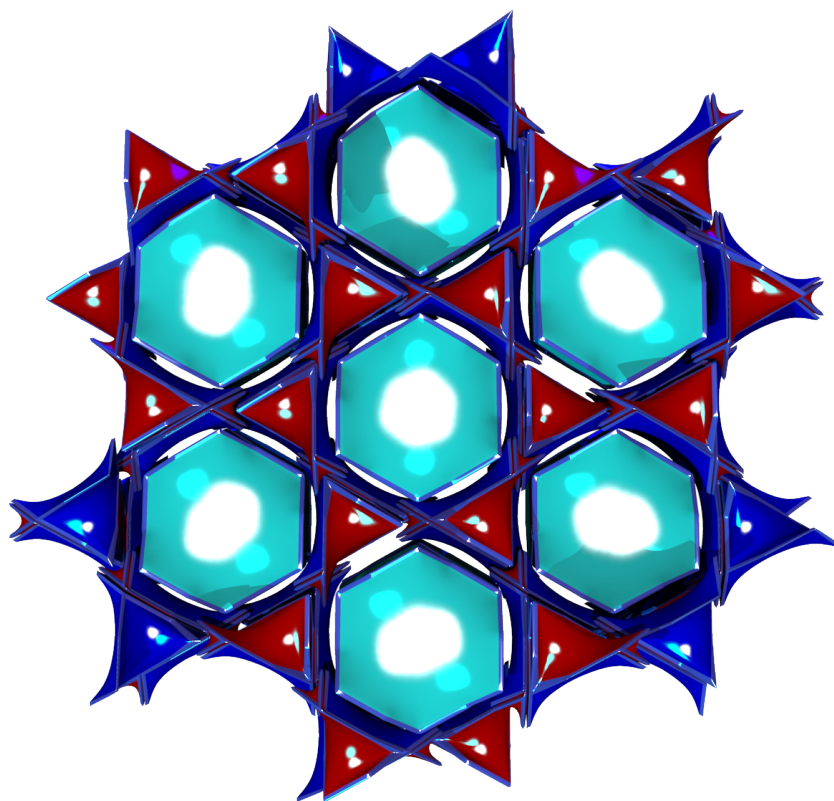


Fig. S6: Tiling of MIL-144 viewed along $[001]$. Tiles: $3[4^2.8^2.] + 3[4.8^3] + [4^3.8^3..12^2]$.
Transitivity: $[2353]$.

5 XRPD patterns of as-synthesized samples

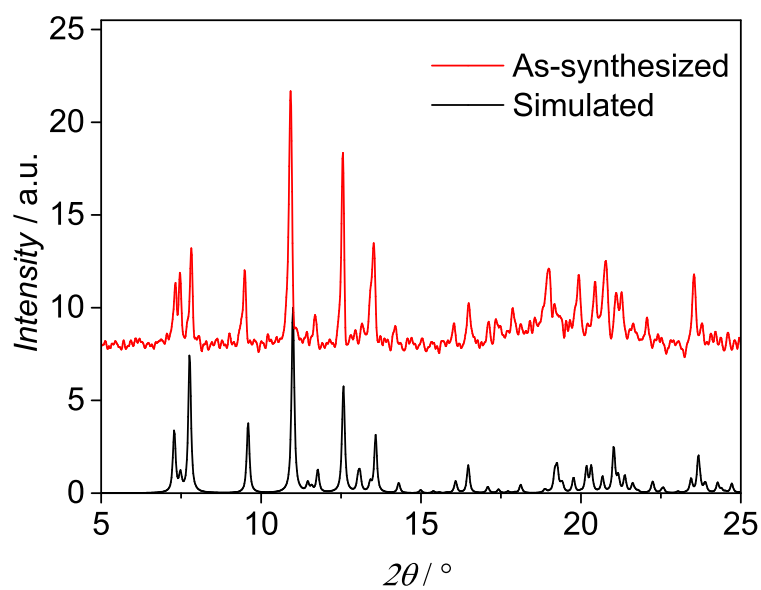


Fig. S7: XRPD pattern for JUMP-2.

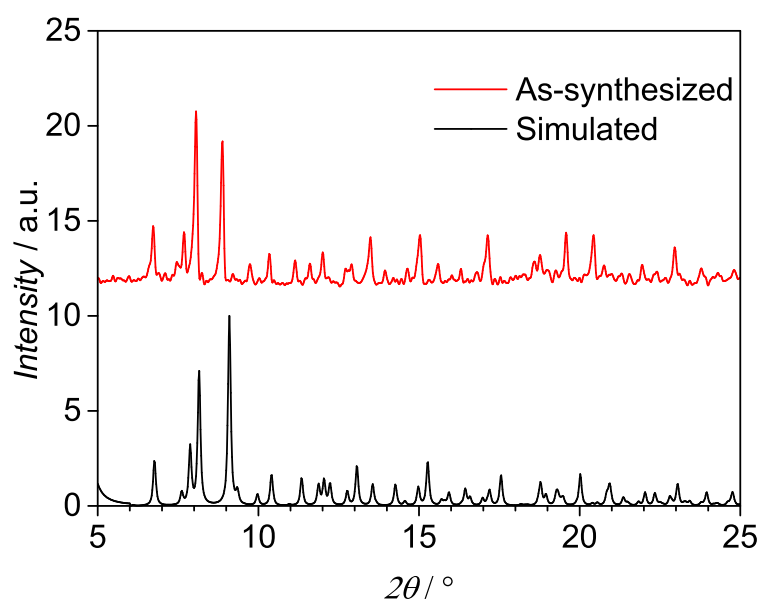


Fig. S8: XRPD pattern for MIL-144.

6 TGA profiles

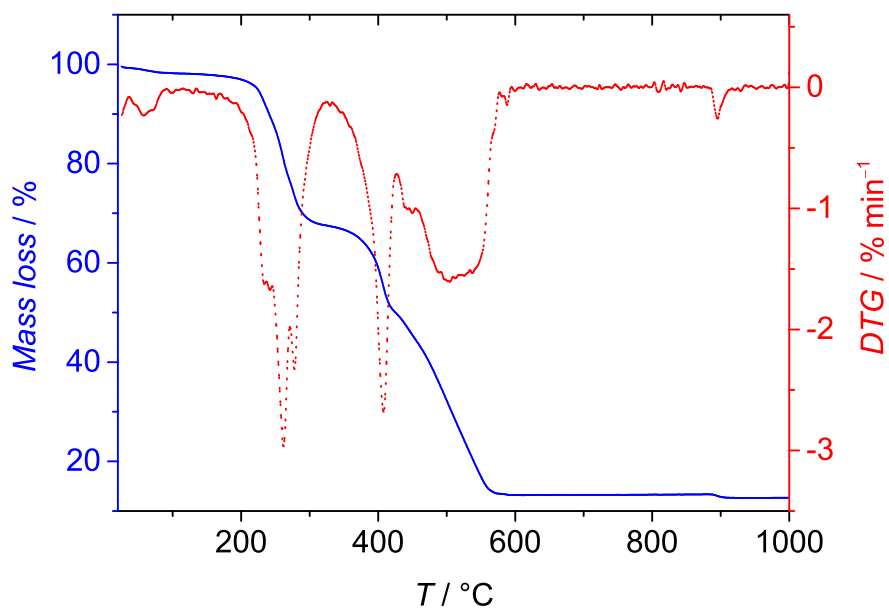


Fig. S9: TGA profile for JUMP-2.

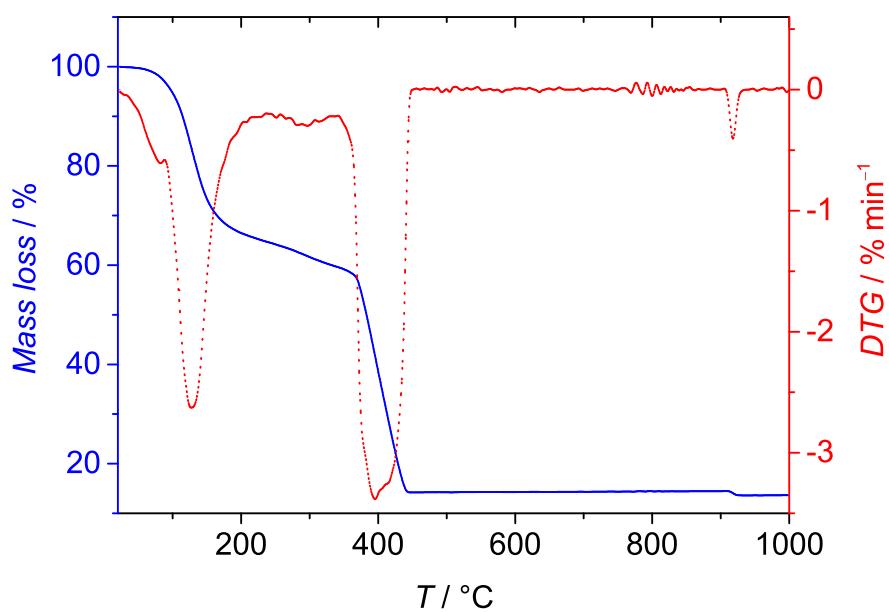


Fig. S10: TGA profile for MIL-144.

7 Alternating current (ac) magnetic measurements for JUMP-2

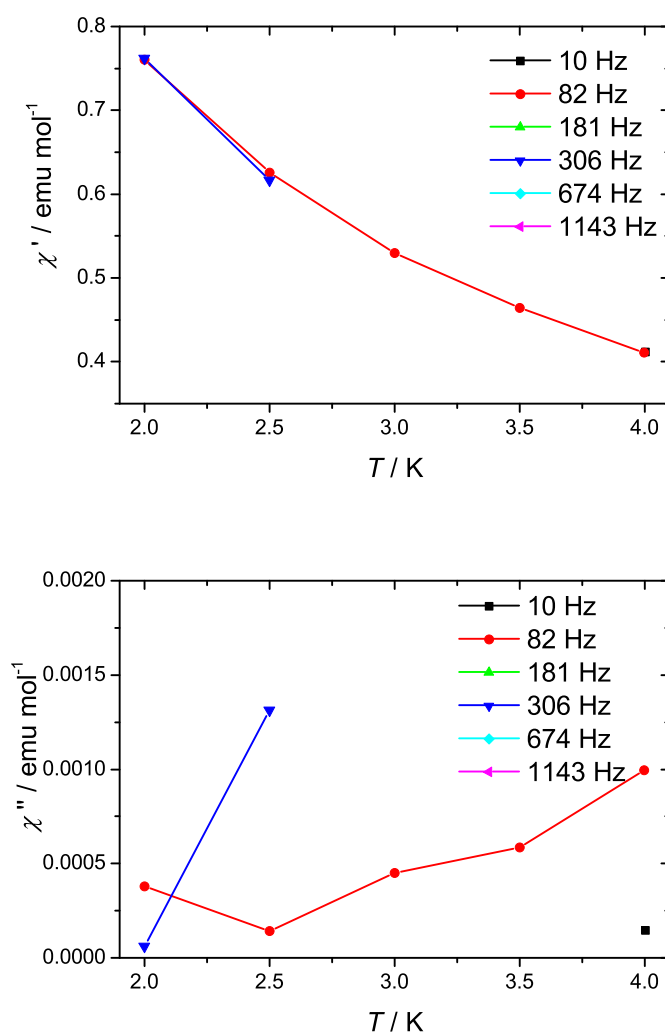


Fig. S11: Temperature dependence of the real (top) and imaginary (bottom) part of the susceptibility for JUMP-2 at a dc field of 0 Oe.

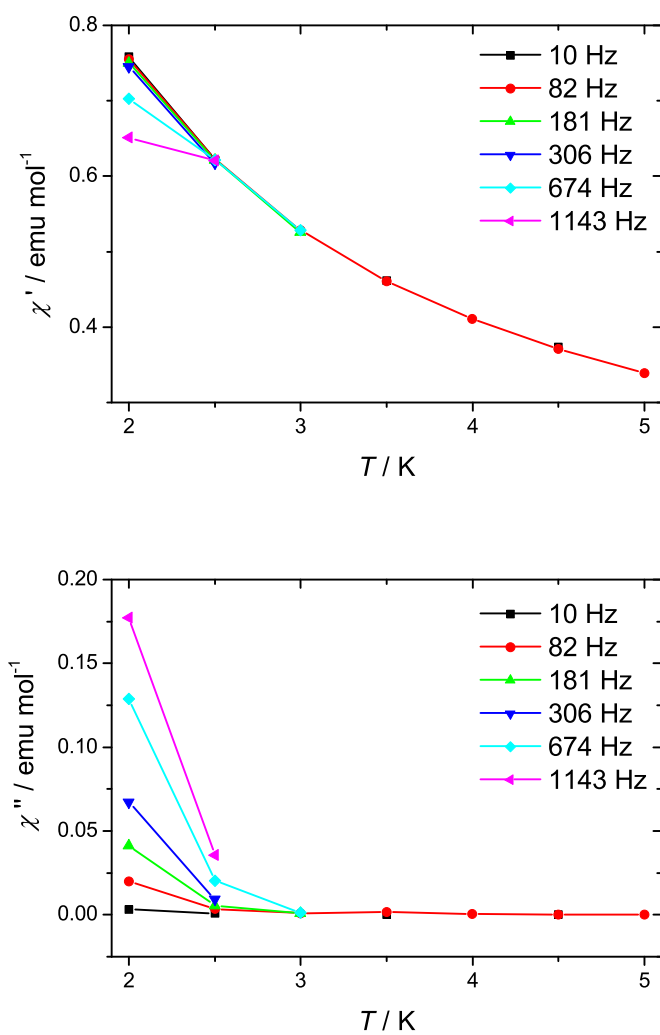


Fig. S12: Temperature dependence of the real (top) and imaginary (bottom) part of the susceptibility for JUMP-2 at a dc field of 400 Oe.

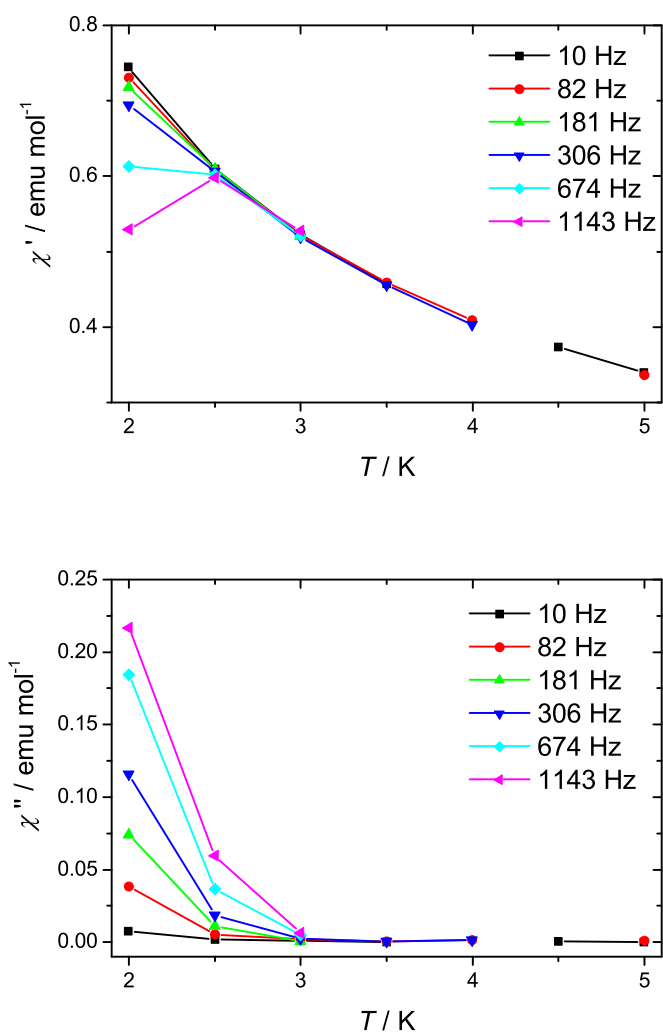


Fig. S13: Temperature dependence of the real (top) and imaginary (bottom) part of the susceptibility for JUMP-2 at a dc field of 1000 Oe.

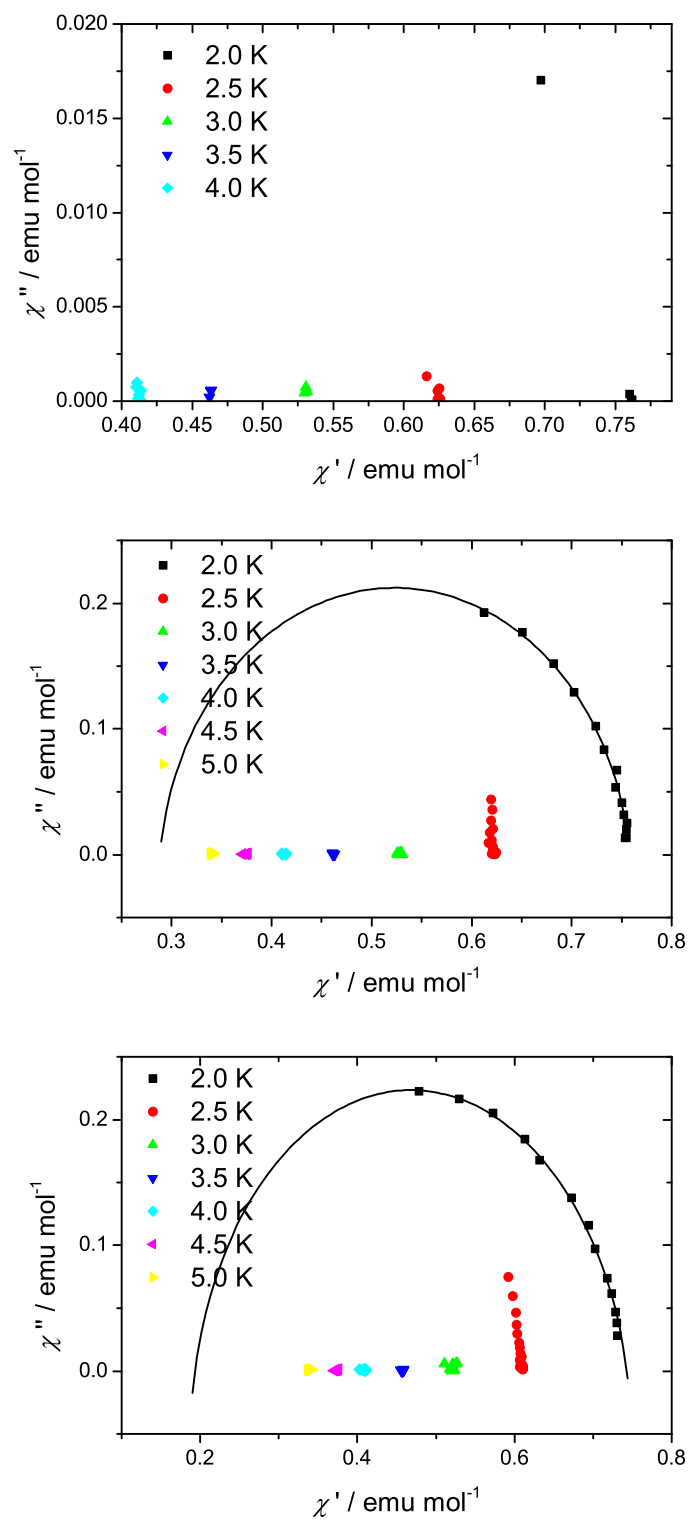


Fig. S14: Cole-cole plots for JUMP-2 at 0 Oe (top) 400 Oe (middle), and 1000 Oe (bottom).

8 Magnetization data for MIL-144

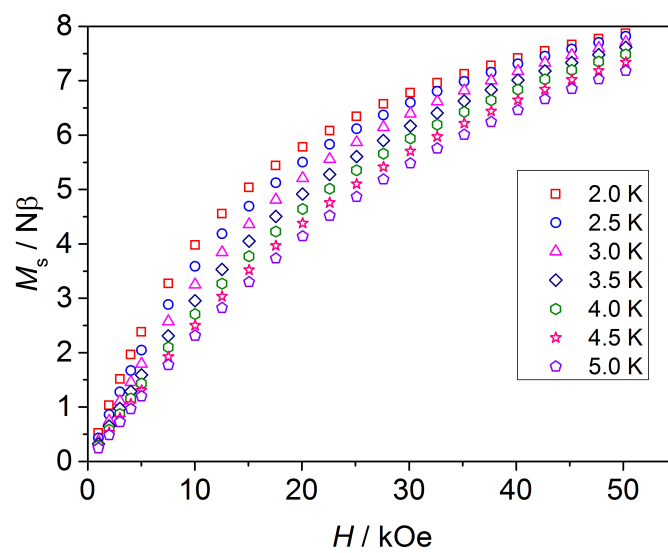


Fig. S15: Temperature- and field-dependent magnetization data for MIL-144.

9 XRPD patterns for cation exchanged samples

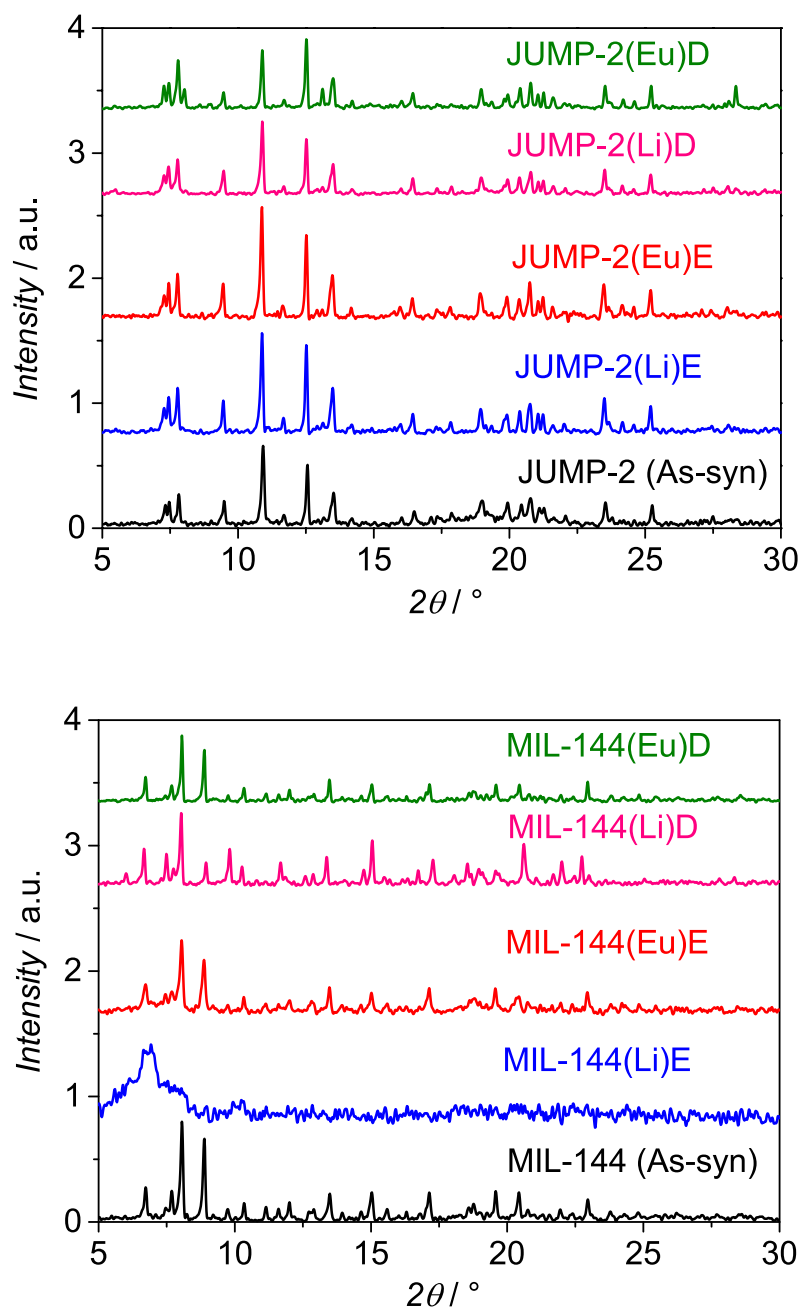


Fig. S16: XRPD patterns for the as-synthesized and cation exchanged samples of both JUMP-2 (top) and MIL-144 (bottom).

10 Fluorescence monitored europium(III) exchange

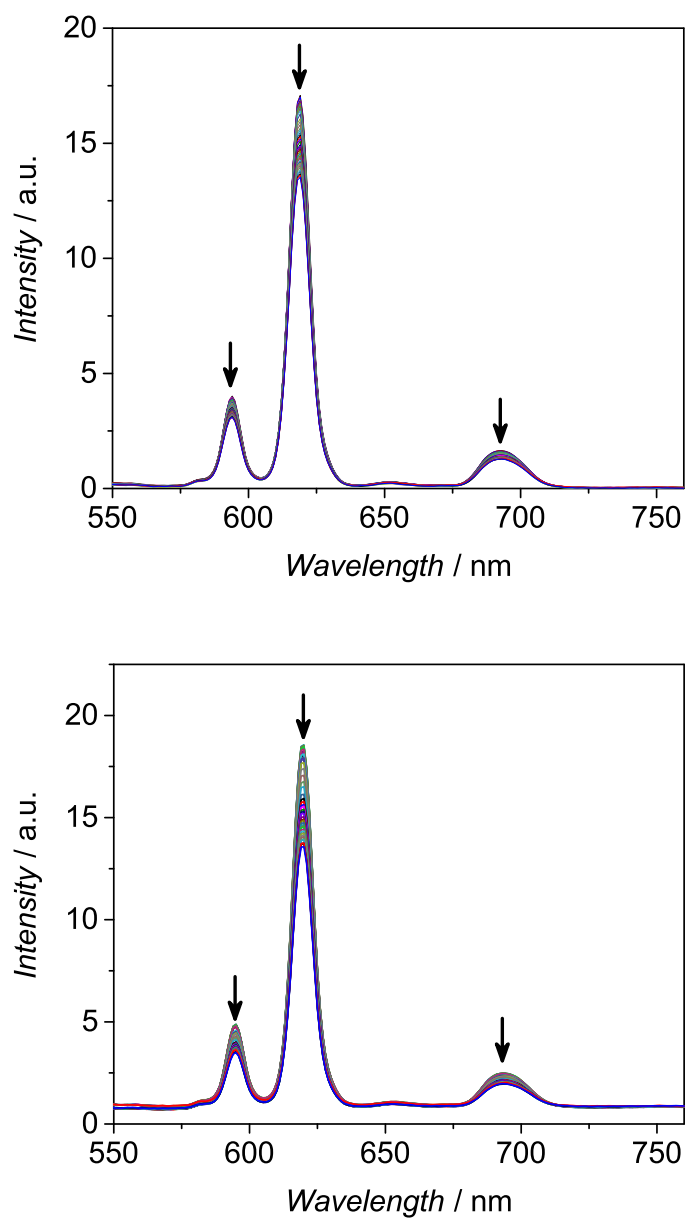


Fig. S17: Cation exchange experiment for JUMP-2 (top) and MIL-144 (bottom) with europium(III) nitrate in ethanol. Fluorescence spectra depicted were measured in time intervals of 1 h over a period of 48 h at an excitation wave length of 395 nm.

11 Sorption data

Table S5: Consistency criteria derived from measured BET Data for the as-synthesized and lithium ion exchanges samples of JUMP-2 and MIL-144 after application of supercritical drying with CO₂

	P/P_o range	C	V_m [cm ³ /g]	$1/\sqrt{C} + 1$	$P/P_o(V_m)$	$a(\text{BET})$ [m ² /g]	R
JUMP-2 ^{scd}	0.13 - 0.28	7	2.99	0.27	0.27	13	0.999
JUMP-2(Li)D ^{scd}	0.13 - 0.30	7	5.40	0.27	0.27	24	0.997
JUMP-2(Eu)D ^{scd}	0.05 - 0.15	147	49.64	0.08	0.08	216	0.999
MIL-144 ^{scd}	0.13 - 0.28	16	4.84	0.20	0.20	21	0.999
MIL-144(Li)E ^{scd}	0.005 - 0.08	1491	86.96	0.03	0.03	380	0.999
MIL-144(Eu)E ^{scd}	0.005 - 0.08	1911	44.43	0.02	0.02	194	0.999

12 Quantum mechanical calculations

12.1 Computational details.

For all atoms the triple- ζ basis set def2-TZPV proposed by Ahlrichs et al.¹ was used. Calculations were performed for molecular models with the position of the non-hydrogen atoms taken from the crystal structures and the positions of the hydrogen atoms were optimized. These optimizations were carried out using the B88 exchange functional² and the correlation functionals VWN(V)³ and P86.⁴ The geometry optimizations were accelerated further by employing the resolution of identity approximation. The CASSCF,⁵ CASPT2,⁶ and RASSI-SO⁷ calculations were carried out for the aforementioned model systems with optimized hydrogen atoms employing the MOLCAS 7.8 package.⁸ ANO-RCC type basis sets⁹ were used for all atoms (contractions: Co-6s5p4d2f1g, coordinating O and N-4s3p2d1f, peripheral N and C-3s2p, H-2s). To save computational time and disk space, the Choleski decomposition was used. Calculations for cobalt(II) involved a (7,10) active space with a double d-set of orbitals. 10 quartet states and 40 doublet states were calculated within the CASSCF procedure to account for all states arising from the d^7 configuration. CASPT2 calculations were done on all quartet states and on the 12 lowest doublet states. Otherwise, intruder states were regularly encountered. RASSI-SO calculations were performed on the CASPT2 wave functions for the states calculated. Calculations of the magnetic properties for mononuclear complexes were performed using the SINGLE_ANISO module.¹⁰

12.2 Magnetic anisotropy for JUMP-2

Quantum mechanical investigations on the electronic structure of the single cobalt(II) ions in JUMP-2 were performed by utilizing multiconfigurational wave function theory within the CASSCF/CASPT2/RASSI-SO methodology. For these calculations the approximation of the cobalt(II) environment is based on a cutout of the infinite two-dimensional layer from the crystal structure of JUMP-2 which is depicted in Figure S18. The CASSCF and CASPT2 energies summarized in Table S6 and their comparison shows only moderate changes upon inclusion of dynamic correlation. The ground state is separated by 3260 cm^{-1} from the first excited spin-free state and resembles the expected A_2 ground term, while the excited T_2 and T_1 term are split due to the deviation from T_d symmetry. Doublet states are found to follow above 16000 cm^{-1} , which confirms the high-spin ground state suggested by experiment. Calculations of the spin-orbit states furthermore show a rather weak mixing of the spin-free ground state with excited states, with a leading weight of over 0.97. This also leads to a small energy gap of 25 cm^{-1} with respect to the first excited Kramers doublet (KD). In addition the g elements obtained for the ground state KD show considerable rhombic

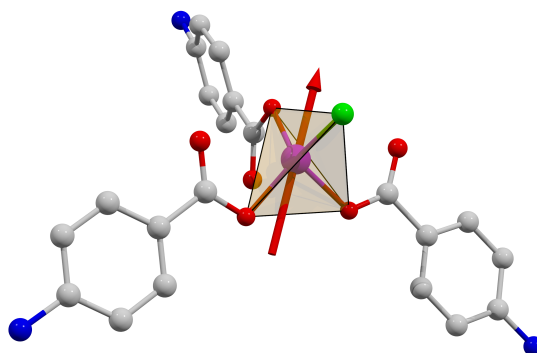


Fig. S18: Representation of the main anisotropy axis of the ground state Kramers doublet derived from multiconfigurational calculations on JUMP-2 for the depicted model structure. Hydrogen atoms are omitted for clarity.

components of over 0.8 (Table S7). Zero-field splitting (ZFS) parameters calculated with the SINGLE_ANISO program reveal easy-axis anisotropy ($D = -11.9 \text{ cm}^{-1}$), however, with a significant rhombic distortion of $E = -1.7 \text{ cm}^{-1}$. In fact, these parameters can reproduce the experimental magnetization data as shown in Figure S19 and are consistent with the presence of efficient relaxation processes already seen from the experimental absence of a relevant single-ion magnet behavior for JUMP-2.

Table S6: Spin-free CASSCF and CASPT2 energies (cm^{-1}) of the quartet and doublet states for JUMP-2. To avoid intruder states, only the 12 lowest doublet states were included in the CASPT2 calculations

	CASSCF	CASPT2
quartet states	0	0
	2853	3260
	3841	4018
	4536	4419
	5254	5621
	7303	8093
	7925	8905
	20589	17524
	21853	18829
	22544	19663
doublet states	19376	16914
	19664	17202
	20149	17637
	20215	17661
	20567	18121
	21277	18953
	22204	19849
	22492	20424
	22985	20823
	25420	22817
	25774	23198
	26152	23758
	...	

Table S7: Energies and g values of the lowest KDs of JUMP-2 calculated with the CASPT2/RASSI-SO procedure

KD		E (cm^{-1})	g value
1	g_1	0	0.8605
	g_2		1.0064
	g_3		7.0316
2	g_1	25	2.2564
	g_2		3.5240
	g_3		5.3774

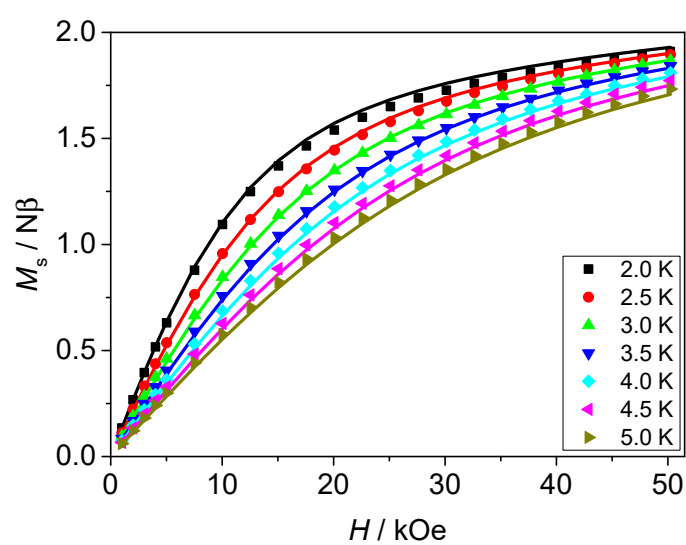


Fig. S19: Temperature- and field-dependent magnetization data for JUMP-2. Lines represent the simulated data based on the parameters obtained from CASPT2/RASSI-SO calculations.

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